

# Phase Relations in the $\text{Li}_2\text{O-V}_2\text{O}_3\text{-V}_2\text{O}_5$ System at 700 °C: Correlations with Magnetic Defect Concentration in Heavy Fermion $\text{LiV}_2\text{O}_4$

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The phase relations in the  $\text{Li}_2\text{O-V}_2\text{O}_3\text{-V}_2\text{O}_5$  ternary system at 700 °C for compositions in equilibrium with  $\text{LiV}_2\text{O}_4$  are reported. This study clarified the synthesis conditions under which low and high magnetic defect concentrations can be obtained within the spinel structure of  $\text{LiV}_2\text{O}_4$ . We confirmed that the  $\text{LiV}_2\text{O}_4$  phase can be obtained containing low (0.006 mol%) to high (0.83 mol%) magnetic defect concentrations  $n_{\text{defect}}$  and with consistently high magnetic defect spin  $S$  values between 3 and 6.5. The high  $n_{\text{defect}}$  values were obtained in the  $\text{LiV}_2\text{O}_4$  phase in equilibrium with  $\text{V}_2\text{O}_3$ ,  $\text{Li}_3\text{VO}_4$ , or  $\text{LiVO}_2$  and the low values in the  $\text{LiV}_2\text{O}_4$  phase in equilibrium with  $\text{V}_3\text{O}_5$ . A model is suggested to explain this correlation.

## I. INTRODUCTION

Heavy fermion (HF) behavior has mostly been seen in  $f$ -electron metals. Such compounds are called heavy fermions because in these materials the current carriers behave as if they have a large mass ( $\sim 10^2\text{--}10^3$  times the free electron mass).  $\text{LiV}_2\text{O}_4$ , first synthesized by Reuter and Jaskowsky,<sup>1</sup> is one of the few  $d$ -electron compounds to show HF behaviour at low temperatures.<sup>2,3</sup>  $\text{LiV}_2\text{O}_4$  has the face-centered-cubic spinel structure with the space group  $Fd\bar{3}m$ . The V atoms are coordinated by six O atoms in slightly distorted octahedron. The Li atoms are coordinated with four O atoms in a tetrahedron. The Li atoms are located in the gaps between chains of the  $\text{VO}_6$  edge-sharing octahedra. From NMR measurements done on  $\text{LiV}_2\text{O}_4$  samples it has been found that for magnetically pure samples the  $^7\text{Li}$  nuclear spin-lattice relaxation rate  $1/T_1$  is proportional to temperature  $T$  at low temperatures (the Korringa law) which is typical for Fermi liquids.<sup>2,4,5</sup> However for samples which contain magnetic defects within the spinel structure, the relaxation rate has a peak at  $\sim 1$  K and also shows other signatures which do not agree with the behavior of Fermi liquids.<sup>6</sup> The occurrence of magnetic defects is easily seen as a low- $T$  Curie-like upturn in the magnetic susceptibility rather than becoming nearly independent of  $T$  below  $\sim 10$  K as observed for the intrinsic behavior.<sup>7</sup> The mechanism for the formation of the magnetic defects is not known yet.

Previously, polycrystalline samples of  $\text{LiV}_2\text{O}_4$  had been prepared from the starting materials  $\text{Li}_2\text{CO}_3$ ,  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  at 700 °C. Typically, the samples contain a concentration of magnetic defects  $n_{\text{defect}}$  within the structure of the spinel phase, ranging from  $\lesssim 0.01$  to 0.7 mol%.<sup>7</sup> Magnetization  $M$  versus applied magnetic field  $H$  measurements at low  $T$  were carried out to estimate  $n_{\text{defect}}$  and the defect spin  $S_{\text{defect}}$ . Low concentrations of defects were found in samples of  $\text{LiV}_2\text{O}_4$  containing small amounts of  $\text{V}_3\text{O}_5$  impurity phase while high defect concentrations were found in samples containing  $\text{V}_2\text{O}_3$  impurity phase.<sup>7</sup> Though the reason behind this correlation is not known yet, these results pointed towards a

controllable way to vary the magnetic defect concentration within the spinel structure. However, it was not clear that the above-noted  $\text{V}_2\text{O}_3$  and  $\text{V}_3\text{O}_5$  impurity phases were in equilibrium with the  $\text{LiV}_2\text{O}_4$  spinel phase at 700 °C. In addition, it was unknown (in Ref. [7]) how the magnetic defect concentration in the spinel phase  $\text{LiV}_2\text{O}_4$  varied if other impurity phases were present. To help resolve these questions, we report here the phase relations in the  $\text{Li}_2\text{O-V}_2\text{O}_3\text{-V}_2\text{O}_5$  system at 700 °C, in the vicinity of the composition  $\text{LiV}_2\text{O}_4$ , and report the magnetic properties of a selection of such compositions.

There have been some studies of the  $\text{Li}_2\text{O-V}_2\text{O}_5$  system which revealed the existence of three phases in the system, namely  $\text{LiVO}_3$ ,  $\text{Li}_3\text{VO}_4$  and  $\text{LiV}_3\text{O}_8$ . Reisman et al.<sup>8</sup> reported the existence of the congruently melting phases  $\text{LiVO}_3$  (reported as  $\text{Li}_2\text{O-V}_2\text{O}_5$ ) and  $\text{Li}_3\text{VO}_4$  (reported as  $3\text{Li}_2\text{O-V}_2\text{O}_5$ ) with melting points 616 °C and 1152 °C, respectively.  $\text{LiV}_3\text{O}_8$  has been reported to be both congruently melting and incongruently melting.<sup>8,9,10</sup> Manthiram et al.<sup>11</sup> reported that  $\text{Li}_{1-x}\text{VO}_2$  is single phase in the compositional range  $0 \leq x \leq 0.3$  at 650 °C.  $\text{LiV}_2\text{O}_4$  was reported to exist in equilibrium with the compounds  $\text{VO}_2$  and  $\text{Li}_{1-x}\text{VO}_2$  from room temperature to 1000 °C by Goodenough et al.<sup>12</sup> The lithium vanadium oxide system  $\text{Li}_x\text{V}_2\text{O}_5$ , also known as the lithium vanadium bronze phase, was reported to exist in a number of single-phase regions for  $0 < x < 1$  and temperature  $T < 500$  °C.<sup>13</sup>

The  $\text{V}_2\text{O}_3\text{-V}_2\text{O}_5$  binary system has been extensively studied and a large number of phases have been reported. Hoschek and Klemm<sup>14</sup> first studied the system and suggested the presence of the phase  $\text{V}_2\text{O}_3$ , the  $\beta$ -phase ( $\text{VO}_{1.65}\text{--VO}_{1.80}$ ), the  $\alpha$ -phase ( $\text{VO}_{1.80}\text{--VO}_2$ ), and the  $\alpha'$ -phase ( $\text{VO}_{2.09}\text{--VO}_{2.23}$ ). Andersson<sup>15</sup> reported phases with general formula  $\text{V}_n\text{O}_{2n-1}$  with  $3 \leq n < 9$ . Additional phases reported in this system are  $\text{V}_9\text{O}_{17}$  and  $\text{V}_{10}\text{O}_{19}$ .<sup>16</sup> The phases with general formula  $\text{V}_n\text{O}_{2n-1}$  with  $3 \leq n \leq 9$  are called the Magnéli phases.<sup>17</sup> The triclinic structure of the Magnéli phases have been reported.<sup>15,16,18,19</sup> The other V-O phases existing between  $\text{VO}_2$  and  $\text{V}_2\text{O}_5$  are  $\text{V}_6\text{O}_{13}$ ,<sup>15,20</sup>  $\text{V}_4\text{O}_9$ <sup>21</sup> and  $\text{V}_3\text{O}_7$ .<sup>22,23</sup> Combined with the work by Kachi and Roy<sup>24</sup>,



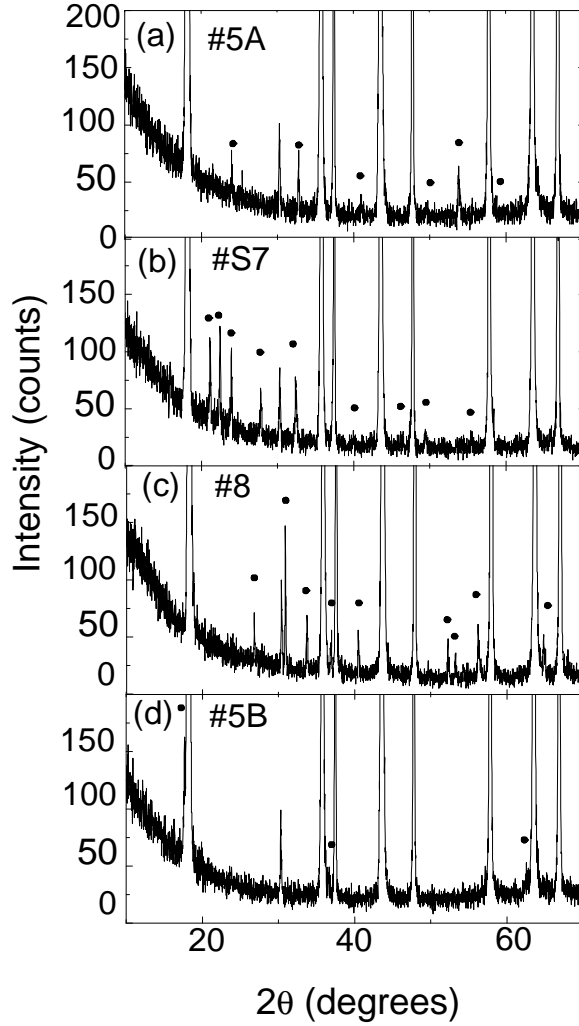


FIG. 2: Expanded X-ray diffraction patterns of samples with compositions near  $\text{LiV}_2\text{O}_4$ . The impurity phase peaks are marked by solid circles. (a) Sample 5A has  $\text{V}_2\text{O}_3$  impurity phase. (b) Sample S7 has  $\text{Li}_3\text{VO}_4$  impurity phase. (c) Sample 8 has  $\text{V}_3\text{O}_5$  impurity phase. (d) Sample 5B has  $\text{LiVO}_2$  impurity phase.

terns of these samples.

The observed magnetic susceptibility  $\chi_{\text{obs}}$  versus  $T$  plots from  $T = 1.8$  K to 350 K at magnetic field  $H = 1$  T for the five samples are shown in Fig. 4 where  $\chi_{\text{obs}} \equiv M_{\text{obs}}/H$ . It can be clearly seen that the dependence of  $\chi_{\text{obs}}$  on  $T$  for the five samples is similar Curie-Weiss like for  $T > 50$  K. However for  $T < 50$  K the dependence is strikingly different. Sample 8 containing  $\text{V}_3\text{O}_5$  impurity phase shows a broad peak at  $T \approx 20$  K, which is characteristic of the intrinsic behavior of magnetically pure  $\text{LiV}_2\text{O}_4$ .<sup>7</sup> Sample 6B which is crystallographically pure also shows a broad peak but it is masked by a Curie-like upturn at  $T < 10$  K. For sample 5A containing  $\text{V}_2\text{O}_3$ , S7 containing  $\text{Li}_3\text{VO}_4$ , and 5B containing  $\text{LiVO}_2$  as impurity phases, the broad peak is totally masked by Curie contributions.

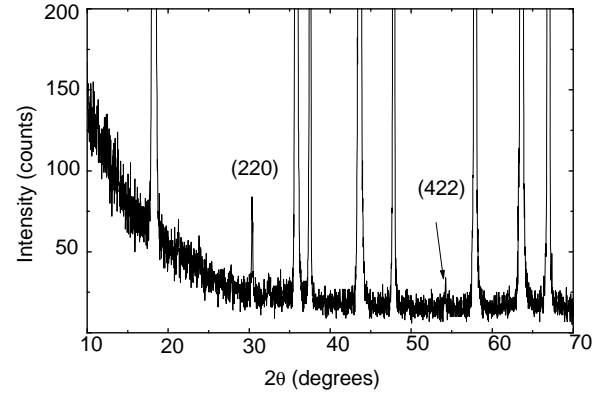


FIG. 3: Expanded X-ray diffraction pattern of the  $\text{LiV}_2\text{O}_4$  sample 6B. The two indexed peaks are of the  $\text{LiV}_2\text{O}_4$  spinel phase. There are no observable impurity phases present.

To interpret the origin of the Curie-like low- $T$  contributions to  $\chi(T)$  of these samples, it is important to consider the potential contributions of the impurity phases to this term.  $\text{V}_3\text{O}_5$  orders antiferromagnetically with its susceptibility showing a very broad maximum between  $T = 120$  K and 130 K<sup>28,29</sup> which is much higher than its Néel temperature  $T_N = 75.5$  K measured by Griffing.<sup>30</sup> The susceptibility for  $T < T_N$  decreases with decreasing  $T$ , has a value  $< 2 \times 10^{-5} \text{ cm}^3/\text{mol}$  at the lowest temperatures, and shows no evidence for a Curie-like term.  $\text{V}_2\text{O}_3$  has a Curie-Weiss-like behaviour for  $T > 170$  K where it is also metallic. Below 170 K it orders antiferromagnetically at a metal to insulator transition and the susceptibility remains constant at about  $5 \times 10^{-4} \text{ cm}^3/\text{mol}$  down to  $T \sim 80$  K. For  $T < 80$  K, the susceptibility decreases with decreasing  $T$  with no sign of a Curie-like upturn.<sup>29,31</sup> The susceptibility of  $\text{V}_{2-y}\text{O}_3$  shows a peak at low  $T$  ( $\sim 10$  K) as it undergoes antiferromagnetic ordering at around 10 K with no evidence for a Curie-like term at lower  $T$ .<sup>29</sup>  $\text{Li}_3\text{VO}_4$  is nonmagnetic since the vanadium atom is in the +5 oxidation state. The only impurity phase exhibiting a low-temperature Curie-like contribution to its susceptibility is  $\text{Li}_{1-x}\text{VO}_2$ , which shows a Curie-like upturn at  $T < 50$  K due to Li deficiency of about 5%.<sup>32,33</sup> However, the amounts of impurity phases in our  $\text{LiV}_2\text{O}_4$  samples are small ( $< 2$  wt%). Assuming that  $x = 0.05$  in  $\text{Li}_{1-x}\text{VO}_2$  impurity phase,<sup>32</sup> where each Li vacancy induces a  $\text{V}^{+4}$  ( $S = 1/2$ ) defect in that phase, one obtains a Curie constant of  $\simeq 4 \times 10^{-4} \text{ cm}^3 \text{ K}/\text{mol}$ , which is far smaller than observed ( $\sim 0.1 \text{ cm}^3 \text{ K}/\text{mol}$ ) in our sample 5B having  $\text{Li}_{1-x}\text{VO}_2$  impurity phase. Thus we can conclude that the Curie-like upturn in the susceptibility of nearly single-phase  $\text{LiV}_2\text{O}_4$  arises from magnetic defects within the spinel structure of this compound and not from impurity phases, which confirms the previous conclusion of Ref. [7].

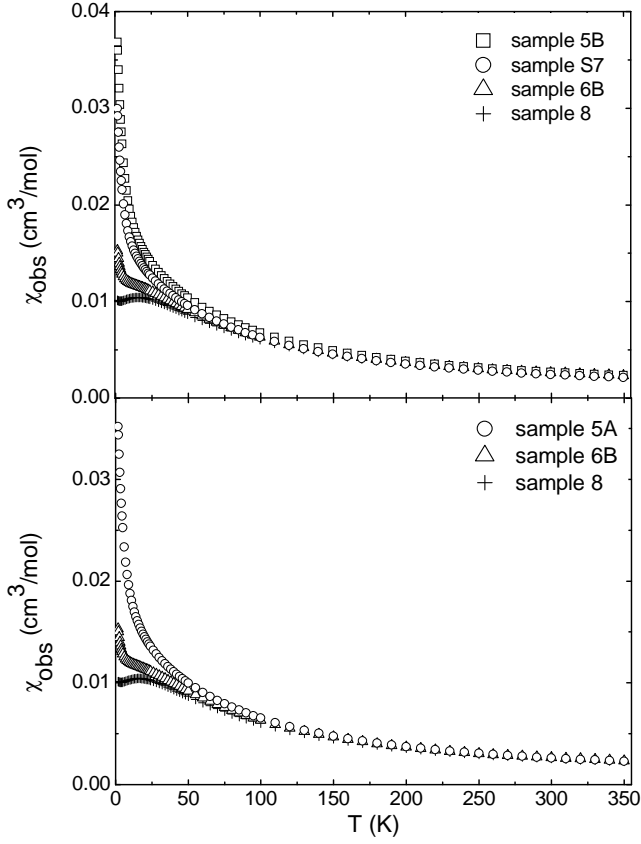


FIG. 4: Observed magnetic susceptibility  $\chi_{\text{obs}}$  versus temperature  $T$  at  $H = 1$  T for several samples in Table I that are nearly single-phase  $\text{LiV}_2\text{O}_4$ .

## 2. Isothermal magnetization measurements

The observed magnetization  $M_{\text{obs}}$  versus applied magnetic field  $H$  isothermal measurements were done at different temperatures between 1.8 K and 350 K with  $H$  varying from 0.001 T to 5.5 T. However, to find  $n_{\text{defect}}$  only the low  $T$  (1.8 K, 2.5 K, 3 K and 5 K) isotherms were used. The  $M_{\text{obs}}$  versus  $H$  curves for different samples at 1.8 K are shown in Fig. 5. The samples showing a Curie-like upturn in the susceptibility show a negative curvature in their  $M_{\text{obs}}$  versus  $H$  curves, whereas the samples having a very small Curie-like upturn in the susceptibility show a hardly observable curvature. This correlation shows that the Curie contribution to the susceptibility is due to field saturable (paramagnetic) defects. The values of the defect concentrations and the values of the defect spins for different samples were determined according to the analysis done by Kondo et al.<sup>7</sup> The observed molar magnetization  $M_{\text{obs}}$  isotherms at low temperatures ( $T \leq 5$  K) for each sample were simultaneously fitted by

$$M_{\text{obs}} = \chi H + n_{\text{defect}} N_A g_{\text{defect}} \mu_B S_{\text{defect}} B_S(x), \quad (1)$$

where  $n_{\text{defect}}$  is the concentration of the magnetic defects,  $N_A$  Avogadro's number,  $g_{\text{defect}}$  the  $g$ -factor of

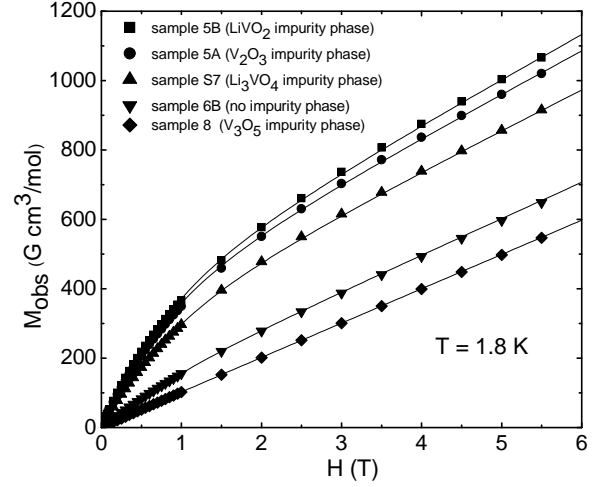


FIG. 5:  $M_{\text{obs}}$  versus  $H$  isotherms of four samples at 1.8 K. The curves passing through the data points are fits by Eq. (1) with the values of the parameters given in Table I.

the defect spins which was fixed to 2 (the detailed reasoning behind this is given in Ref. [7]),  $S_{\text{defect}}$  the spin of the defects,  $B_S(x)$  the Brillouin function, and  $\chi$  the intrinsic susceptibility of  $\text{LiV}_2\text{O}_4$  spinel phase. The argument of the Brillouin function  $B_S(x)$  is  $x = g_{\text{defect}} \mu_B S_{\text{defect}} H / [k_B (T - \theta_{\text{defect}})]$  where  $\theta_{\text{defect}}$  is the Weiss temperature. The four fitting parameters  $\chi$ ,  $n_{\text{defect}}$ ,  $S_{\text{defect}}$  and  $\theta_{\text{defect}}$  for each sample are listed in Table I. Since the parameters  $n_{\text{defect}}$  and  $S_{\text{defect}}$  are strongly correlated in the fits, the products of these are also listed in Table I.

The grain sizes of our samples were studied using a scanning electron microscope (SEM). The SEM pictures of some of our samples are shown in Fig. 6. As seen from the figure, the grain sizes are 1 – 10  $\mu\text{m}$ , and from Table I there is no evident correlation between the sample grain sizes and the magnetic defect concentrations.

## IV. SUGGESTED MODEL

The reason behind the correlation between the presence of the Li-V-O and V-O phases and the variation of the magnetic defect concentration in  $\text{LiV}_2\text{O}_4$  is not known yet. We speculate that this is due to the formation of vacancies and/or interstitials in the spinel structure due to the variation of the sample composition from the ideal stoichiometry. A possible model is shown in Fig. 7. The black triangle is stoichiometric  $\text{LiV}_2\text{O}_4$  while the circular region is a small ( $\lesssim 1$  at.%) homogeneity range of  $\text{LiV}_2\text{O}_4$ . Based on this model, the  $\text{LiV}_2\text{O}_4$  phase in the samples having  $\text{V}_3\text{O}_5$  impurity phase are very close to the ideal stoichiometric  $\text{LiV}_2\text{O}_4$ , the magnetic susceptibility is the intrinsic susceptibility for the ideal stoichiometric spinel phase and the magnetic defect concentration is very small. The composition of the spinel phase in samples having  $\text{V}_2\text{O}_3$ ,  $\text{Li}_3\text{VO}_4$  or  $\text{LiVO}_2$  as impurity

TABLE I: Results of the analyses of the  $M_{\text{obs}}(H, T)$ . The error in the last digit of a parameter is given in parentheses.

Sample no	Impurity	$\chi$ (cm <sup>3</sup> /mol)	$n_{\text{defect}}$ (mol%)	$S_{\text{defect}}$	$\theta_{\text{defect}}$ (K)	$n_{\text{defect}}S_{\text{defect}}$ (mol%)
5A	V <sub>2</sub> O <sub>3</sub>	0.0123(1)	0.77(3)	4.0(1)	-0.70(13)	3.08(13)
S7	Li <sub>3</sub> VO <sub>4</sub>	0.0115(1)	0.67(2)	3.7(1)	-0.59(9)	2.52(8)
8	V <sub>3</sub> O <sub>5</sub>	0.0098(1)	0.0067(28)	6.3(27)	-1.0(10)	0.04(18)
5B	LiVO <sub>2</sub>	0.0127(2)	0.83(3)	3.9(1)	-0.65(12)	3.29(13)
6B	no impurity	0.0104(1)	0.21(1)	3.5(2)	-0.75(13)	0.73(4)

phases deviates from the ideal stoichiometry as can be seen in the figure. This variation from the ideal stoichiometry would cause the above vacancies and/or interstitial defects to form which in turn cause the formation of paramagnetic defects. The samples having chemical composition different from the black solid triangle (i.e. the ideal stoichiometric composition) but within the circular region will be by definition single phase LiV<sub>2</sub>O<sub>4</sub> but not having the ideal stoichiometry. Thus some samples of LiV<sub>2</sub>O<sub>4</sub> will have magnetic defects even if there are no impurity phases in them which might be the case for our sample 6B and also samples 3 and 7 studied by Kondo et al.,<sup>7</sup> where some samples were essentially impurity free but still had a strong Curie contribution in their susceptibility.

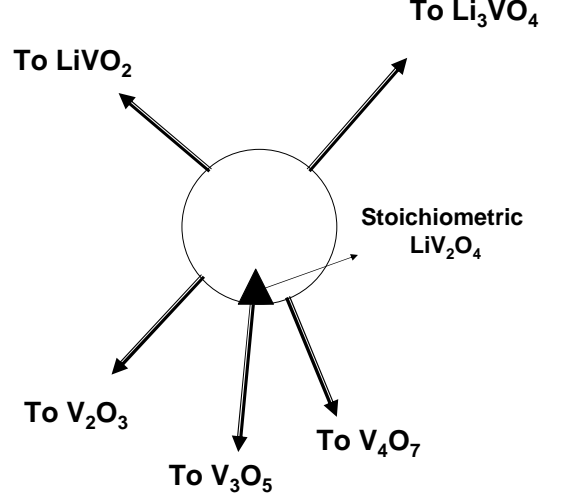


FIG. 7: Suggested model for the mechanism of the crystal and magnetic defect formation in LiV<sub>2</sub>O<sub>4</sub>. The figure shows an enlarged region around LiV<sub>2</sub>O<sub>4</sub> in the phase relation picture (Fig. 1) where the circle represents a possible small homogeneity range of the spinel phase and the filled triangle is stoichiometric LiV<sub>2</sub>O<sub>4</sub>.

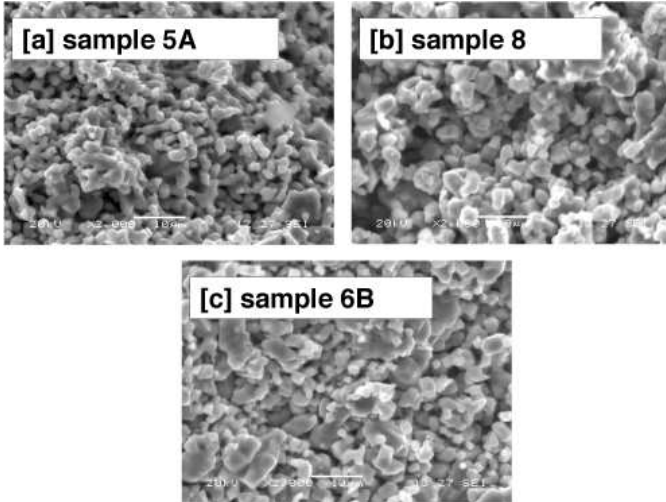


FIG. 6: SEM pictures of our LiV<sub>2</sub>O<sub>4</sub> powder samples. No evident correlation between the grain sizes and the defect concentrations was found. The bars at the bottom of each picture are 10  $\mu\text{m}$  long. The grain sizes are in the range 1 to 10  $\mu\text{m}$ .

## V. CONCLUSION

In this paper we have reported the phase relations in the Li<sub>2</sub>O-V<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> system at 700 °C for compositions in equilibrium with LiV<sub>2</sub>O<sub>4</sub>. This study helped us to determine the synthesis conditions under which polycrystalline samples of LiV<sub>2</sub>O<sub>4</sub> could be prepared with variable magnetic defect concentrations ranging from  $n_{\text{defect}} = 0.006$  to 0.83 mol%. High magnetic defect concentrations were found in samples containing V<sub>2</sub>O<sub>3</sub>, Li<sub>3</sub>VO<sub>4</sub>, or LiVO<sub>2</sub> impurity phases while the samples containing V<sub>3</sub>O<sub>5</sub> impurity phase had low defect concentration. We suggested a possible model which might explain this correlation. Our work shows how to systematically and controllably synthesize LiV<sub>2</sub>O<sub>4</sub> samples with variable magnetic defect concentrations within the spinel structure. The results should be helpful to other researchers synthesizing samples for study of the physical properties of this system.

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